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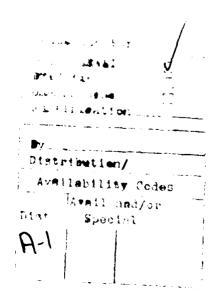All other editions are obsolete.

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DIFFUSION OF CAMPHORQUINONE IN

UNIAXIALLY DRAWN POLYCARBONATE FILMS

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Abstract

Employing the laser induced holographic grating relaxation technique, we have measured tracer diffusion coefficients of a phtochromous dye, camphorquinone (CQ), in uniaxially drawn polycarbonate films as a function of stretch ratio. Anisotropy in the tracer diffusion coefficient has been observed with $D_{||}$ greater than $D_\perp$ by at least a factor of 4 for the film stretched to the stretch ratio $\delta = 2.3$. The diffusion coefficient along the direction of stretch $D_{||}$ increases significantly with increasing δ, whereas $D_\perp$ decreases slightly with increasing δ. The stretch ratio dependence of $D_{||}$ and $D_\perp$ is interpreted according to a modified free volume theory. The strain rate and stretch temperature dependence of the anisotropic tracer diffusion coefficient has also been investigated.

Introduction

Translational diffusion of small molecules in a polymer is known to be affected by the sample preparation history of the material. This effect has been demonstrated by measuring the translational diffusion coefficient, D, of either organic or gas molecules in a stretched, compressed or shear banded polymer.[1] Early studies have detected the retardation of diffusion coefficients of small molecules in uniaxially drawn polyethylene[1-5], polypropylene,[6] and other semicrystalline polymers[7]. In both compressed and shear bands of poly(methyl methacrylate) (PMMA)[8,9] the average D value of methanol was found to increase, whereas in the drawn PMMA[9] the average D value decreases. More recently, the methanol diffusion coefficient in uniaxially drawn poly(ether sulphone)[10] was found to increase with increasing draw ratio in the direction perpendicular to the polymer stretching[10]. A similar effect was also observed in the diffusion coefficient of hexane in polystyrene[11]. However, most of the studies conducted thus far were focused primarily on systems of technological applications consisting either of semicrystalline polymers or of small molecules in which the intermolecular interaction, such as hydrogen bonding, is present. Little emphasis is placed on the mechanistic understanding of the diffusion process in stretched amorphous polymers in which chains are oriented.

In this paper, the translational diffusion coefficient of camphorquinone (CQ) in a uniaxially drawn polycarbonate (PC) film is reported. This is a continuation of efforts in our attempt towards understanding the chain orientation effect on diffusion[12] in an amorphous polymer film. The temperature dependence of the translational tracer diffusion coefficients of CQ in pure amorphous PC was published by Wang and co-workers[13,14]. Ehlich and Sillescu[15] also reported the diffusion results of tetrahydrothiophene-indigo in PC. It was shown in ref. 14 that the tracer diffusion coefficient depends sensitively on the sample preparation history, even though no predeformation was induced.

Experimental

Materials and Sample Preparation

Polycarbonate was purchased from the General Electric Co., with the trade name LEXAN-4. The glass transition temperature of the PC is 150°C, as determined by using DSC (Perkin Elmer Delta Series Instrument) with a heating rate of 20°C/min. The weight average molecular weight of LEXAN-4 is 2.27×10^4, with the polydispersity index $Mw/Mn = 2.15$, as characterized by using GPC (Waters) with dichloromethane used as a solvent. To prepare the PC sample for this study, the PC pellet was first dissolved in dichloromethane. The solution was filtered through a 0.02 μm teflon disk filter (Gelman Science) to remove dust. PC was precipitated as powder from the solution by adding methanol (a nonsolvent for PC). The precipitated PC powder was removed and dried under vacuum at 150°C for two days. This process is necessary to remove plasticizers which were added during the manufacturing process of LEXAN-4. As shown in ref. 4, without carrying out this step of the sample preparation, the presence of plasticizers will render the tracer diffusion coefficient D significantly greater. The dried PC powder was mixed with 0.3% (by weight) of CQ (from Aldrich Chemical Co.). The mixture was then thoroughly mixed in a blender. After being mechanically mixed, the PC powder containing CQ was compression molded at 280°C (for about 10 min.) in a hydraulic press into a sheet of 0.07 mm thick. The optically clear PC sheet was then annealed at 200°C for 2 hours and air cooled to room temperature. Tensile test specimens with a gauge length of 36.0 mm and a width of 25.0 mm were cut from the sheets for further experiments.

Instron tensile drawing

Specimens were stretched in a computer interfaced Instron tensile test machine (Instron 4501) equipped with an Instron 3111 oven. The oven was preheated to 155°C as

indicated on a temperature recorder with a thermocouple located near the jaws. The specimen was loaded on the jaws and thermally equilibrated in the oven at the set temperature for about 20 min. The specimen was then stretched at a constant crosshead speed to a preset total elongation. After being stretched, a jet of cold water was sprayed onto the specimen to quench the stretched PC film to room temperature. The specimen was then removed from the jaws with the drawn dimension kept fixed. Specimens were stretched with different strain rates and elongation to produce uniform necks. Samples for tracer diffusion measurements were cut from the most uniform portion of the neck of the stretched specimens.

Diffusion Measurements

The laser induced holographic grating relaxation (HGR) technique was used to measure tracer diffusion coefficients. The holographic grating was induced by crossing two equal intensity coherent beams derived from an argon ion laser (Spectra-Physics, Model 2000) at the wavelength equal to 488.0 nm. The grating was written with the laser, operating at a power of about 40 mW for about 2.0 sec. The crossing angle between two writing beams was varied from $3.6°$ to $15.0°$, corresponding to a grid spacing, $d = \lambda[2\sin(\theta/2)]^{-1}$, varying from 1.87 to 7.77 μm, respectively. The optical setup was the same as that employed in the previous work[13] on the diffusion study of CQ in amorphous PC with no external stretching perturbation. The film was mounted in a rotatory stage; the long axis of the film can be accurately rotated with respect to the laser beams, as shown in Figure 1. At $\alpha = 0°$, the optical grating experiment only samples the CQ molecules diffusing along the direction of stretch ($D_{||}$). On the other hand, at $\alpha = 90°$, it samples those diffusing along the direction perpendicular to stretch ($D_{\perp}$). All of the diffusion coefficients presented in this paper are the average of three measurements.

The dynamic grating diffraction lineshape follows the decay-growth then decay behavior as previously observed in ref 14. Mathematically it can be expressed as:

$$I(t) = (\alpha e^{-t/\tau_1} - \beta e^{-t/\tau_2})^2 \qquad (1)$$

where α and β are positive constants; τ_1 and τ_2 are the relaxation time constants, corresponding to the diffusion coefficient of CQ and its photoproduct (CQP), respectively. While the size of CQ and CQP only differs slightly, the diffusion coefficient of CQ and CQP may differ as much as 10 fold. This result has been interpreted in terms of free volume theory.[13,14] Diffusion coefficients for CQ and CQP can be obtained by first fitting the diffraction curve to Eq. (1) to obtain τ_1 and τ_2, and the diffusion coefficients are then computed by using Eq. (2).

$$D_2 = \frac{\lambda^2}{16\pi^2 \tau_2 \sin^2(\theta/2)} \qquad (2)$$

where λ is the laser wavelength in vacuum and θ is the diffraction angle. However, as shown in our previous work,[16] one may also obtain D_2 (the diffusion coefficient of the larger species, CQP) by analyzing the slow decay portion of the diffraction curve without scarifying much accuracy. This procedure is especially advantageous for extracting very slow diffusion coefficient ($< 10^{-14}$ cm^2/s) in which a long holographic grating reading time (several hours) is generally required. For this work, we first curve fitted the diffraction intensity curve from the unstretched film to Eq. (2); the result was compared and verified by analyzing the second slow decay portion of the diffraction intensity curve. The rest of the samples were then analyzed by simply using the second decay portion of the diffraction intensity I(t) vs. time curves. A more detailed discussion of the LIHGR technique and the data analysis method can be found in the refs. 16-19. In the subsequent section, we shall simply replace D_2 by D.

Results and discussion

Shown in Figure 2 are the diffusion coefficients $D_{||}$ and $D_{\perp}$ of CQP, obtained at 132°C for the samples stretched at 155°C with the strain rate equal to 0.7 min^{-1}, plotted as a function of stretch ratio. For the unstretched film, we have found $D_{||} = D_{\perp} = 3.1 \times 10^{-14}$ cm^2/s, which is in agreement with the diffusion coefficient measured for the amorphous PC pillet with the same sample preparation method.[14] Upon stretching, $D_{||}$ increases steadily with increasing stretching ratio, but $D_{\perp}$ decreases only slightly until up to 130% elongation, beyond which $D_{\perp}$ decreases more with increasing stretching. At 130% elongation, $D_{||}$ increases to nearly three times the unstretched value, and is about a factor of 4 of $D_{\perp}$.

Early studies of the orientation effect on the transport properties of small molecules in semicrystalline polymer fibers have shown that the diffusion coefficient first increases along the direction of stretch, but then decreases with further increasing the stretch ratio[20]. The effect has been interpreted as due to an increase in microvoids and channels or cracks induced by stretching, in addition to polymer relaxation[5]. While the diffusion process in the deformed amorphous polymer is rather complex[8-11], effects due to the increase in free volume, chain relaxation, and induced crazing and crystallization have been considered. Compared to the diffusion data reported in the literature, we found that only the $D_{\perp}$ behavior obtained here is consistent with the diffusion of methanol in drawn PMMA[9]. But our $D_{||}$ results are different from the drawn PMMA result, and also differs from that of hexane in drawn polystyrene[11]; apparently, in addition to chain orientation, both solvent-induced relaxation and crazing also affect the diffusion process of hexane in polystyrene.

In contrast to the mechanism of orientation of the probe molecules associated with the anisotropic thermal diffusion coefficient observed in an aligned liquid crystal,[21] the anisotropic diffusion coefficient of CQP in PC is not associated with the orientation of CQP,

as the shape of CQP is rather spherical. Rather, it is associated with the chain orientation of the polymer host. Uniaxially stretching amorphous PC will result in the orientation of the polymer chains along the direction of stretch; the oriented chains are expected to create an open channel to ease the molecular transport, provided that the average channel width is wider than the size of the diffusant. Hence, we expect that by stretching an amorphous PC film, an increase in the diffusion coefficient in the direction of stretch will result. Furthermore, in an earlier work, we showed by Brillouin scattering[22] that when PC is subject to an uniaxial stress, the sound velocity in the transverse direction is not significantly affected; thus, the insensitivity of $D_\perp$ to stretching was interpreted as due to the lack of orientation in the transverse direction. The fact that the stretch induced crystallization in the amorphous PC film is negligible suggests[23] that the redistribution of free volume due to stretching is the main factor that affects the tracer diffusion coefficient in the PC film, even at the temperature below T_g[14,15].

In free volume theory the tracer diffusion coefficient D is assumed to vary with the fractional free volume, f, according to:[24]

$$D = AT \ exp(-\frac{B_d}{f}) \qquad (3)$$

where A and B_d are constants, and T is temperature. Due to the fact that only a traced amount of CQ molecules is present, f is assumed to be determined only by the PC polymer.

Free volume is directly related to the distribution of various polymer chain conformations. As the polymer is stretched, the chain conformation also undergoes a change to affect free volume. To modify free volume theory to describe the anisotropic translational diffusion process, we assume that before stretching, polymer chains are represented by a collection of spheres with a mean radius equal to the radius of gyration R_g. Upon uniaxially stretching the polymer film, the polymer chain undergoes deformation, and

the sphere becomes an ellipsoid, whose volume is given by $\frac{4\pi}{3} R_{\parallel} R_{\perp}^2$, where $R_{\parallel}$ and $R_{\perp}$

are radii of the major and the minor axis, respectively. The major axis is assumed to be along the direction of stretch. For small stretching ratio there is experimental evidence[25] indicating that the macroscopic stretching ratio δ is equal to $R_{\parallel}/R_g$. If one assumes that the deformation of the polymer chain represented by spheres of radius of gyration R_g, due to external stretching is affine, then it is easy to show that $R_{\perp}/R_g = \delta^{-1/2}$. The affine deformation is justified at small stretching ratio ($\delta < 3$) when the polymer is deformed above T_g, as suggested by Schroeder et al[26], who, by using the small angle neutron scattering (SANS) technique, reported the observation of an affine deformation of stretched polystyrene. Although the affine deformation suggested by Schroeder et al. in PS may not be correct for PC, we shall assume this model to interpret the present observation.

Adopting the above assumption, one will readily note that the deformation will give rise to an increase in the effective fractional free volume along the direction of stretch, $\Delta f_{\parallel}$, given by:

$$\Delta f_{\parallel} = \pi (R_g^2 - R_{\perp}^2) a = \pi R_g^2 a (1 - \delta^{-1}) \tag{4}$$

where a is a constant proportional to the number of chains and the mean distance between two chains in the longitudinal (the stretch) direction. The increase in free volume provides a more open channel to facilitate translational diffusion.

On the other hand, in the transverse direction (the direction perpendicular to the direction of stretch), there is a decrease in the effective fractional free volume because the diffusant now sees ellipsoids with long axes transverse to the direction of diffusion. The change in fractional free volume $\Delta f_{\perp}$ is given by:

$$\Delta f_{\perp} = \pi (R_{||} R_{\perp} - R_s^2) b = \pi R_s^2 b (\delta^{\frac{1}{2}} - 1) \qquad (5)$$

where b is a constant proportional to the number of chains and the mean distance between two chains in the transverse direction. We expect the constant b to be greater than the constant a of Eq. (4) for the reason that the mean distance (i.e. voids) between two chain in the direction transverse to the stretch direction is greater than that along the direction of stretch. This result is consistent with our model of the affine deformation as the deformation affects only the polymer chains, and the space unoccupied by the chains are voids which constitute the free volume.

With the help of Eqs. (4) and (5), we obtain from Eq. (3) expressions for two tracer diffusion coefficients $D_{||}$ and $D_{\perp}$ as:

$$\ln\left(\frac{D_{||}}{D_0}\right) = \frac{\gamma(1-\delta^{-1})}{\beta_{||} + (1-\delta^{-1})} \qquad (6)$$

and

$$\ln\left(\frac{D_{\perp}}{D_0}\right) = \frac{\gamma(1-\delta^{\frac{1}{2}})}{\beta_{\perp} + (1-\delta^{\frac{1}{2}})} \qquad (7)$$

where D_0 is the isotropic tracer diffusion coefficient in the polymer film before it is subject to stretch, and in accordance to Eq (3), it is given by:

$$D_0 = ATexp(-B_d/f_0) \qquad (8)$$

Here f_0 is the fractional free volume of the film before stretch; $\beta_{||}$ and $\beta_{\perp}$ are equal to $f_0/\pi R_g^2 a$ and $f_0/\pi R_g^2 b$, respectively. The quantity γ is equal to B_d/f_0.

The experimental data $D_{||}$ and $D_{\perp}$ as a function of δ are shown in Fig. 2. One notes that $D_{||}$ increases steadily with increasing δ, whereas $D_{\perp}$ decreases only slightly with δ.

These data are fitted to Eqs. (6) and (7) respectively. The fits are given by the solid lines. The curve fitting yields the values of three parameters γ, $\beta_{||}$ and $\beta_\perp$ as γ = 50.0, $\beta_{||}$ = 27.0 and $\beta_\perp$ = 60.7. The fit gives $\beta_\perp/\beta_{||}$ > 1. The value of the γ parameter is larger than that of the Williams-Landel-Ferry (WLF) coefficient C_1^D obtained previously for the CQ diffusion coefficient in PC.[14] Since C_1^D is defined as 2.3 x Bd/$f(T_g)$ where $f(T_g)$ is the fractional free volume at T_g, the larger γ value is consistent with smaller fractional free volume expected at the temperature below T_g at which our measurements were made. This is also consistent with the present assumed model of deformation, as was mentioned above, after the deformation the mean interchain distance in the transverse direction is expected to be greater in the perpendicular direction than in the parallel direction. Equations (6) and (7) thus give a satisfactory description of the experimental results.

To see how the strain rate affects the diffusion behavior, the samples were prepared by drawing at 155°C with different crosshead speeds to reach the same total elongation. For the various strain rates studied, the drawn samples had about the same initial dimension. The neck portion of the stretched sample was cut and used for the diffusion measurement. The change in $D_{||}$ with the strain rate is shown in Figure 3. Within the present strain rate range, $D_{||}$ increases slightly with increasing the strain rate. Since a greater orientation of the polymer chain is induced with a higher strain rate, the increase in the $D_{||}$ value with increasing the strain rate is expected. However, the increase in $D_{||}$ in the present case is somewhat smaller than that of semicrystalline polypropylene,[4] in which the diffusion coefficient of chloroform was found to increase linearly by about an order of magnitude as the strain rate of increased from 0.067 to 0.67 min^{-1}.

The effect of stretching temperature on $D_{||}$ was also investigated. Shown in Figure 4 is the change in $D_{||}$ with the stretching temperature, with the stretching ratio of the film kept at δ = 1.88. Clearly, the rate of chain relaxation increases as the temperature of the

polymer is increased. If the time of quenching the polymer to low temperature is longer than the chain orientational relaxation time, orientation will not be preserved as the film is quenched. This would result in a smaller increase in $D_{||}$ as only a small part of the polymer chain orientation remains oriented. Stretching the polymer film at the temperature far above T_g will result in small chain orientation due to fast chain orientational relaxation. The amount of chain orientation induced by uniaxially drawing will thus depend on the quenching time relative to the relaxation time. As the stretch temperature increases from 140°C to 170°C, at small quench rate, $D_{||}$ was found to decrease with increasing stretch temperature from 8.5×10^{-14} cm^2/s to 3.2×10^{-14} cm^2/s. This stretching temperature effect is also consistent with the time-temperature superposition principle: Higher stretching temperatures are equivalent to lower strain rates, that is, longer times for molecular relaxation during the stretching process. On the other hand, stretching the film below T_g will not yield a uniform increase in orientation, due to the fact that the polymer chain motion is very sluggish below T_g.

One might also make an attempt to further modify Eq. (6) to incorporate the chain deformation kinetic effect into free volume theory by modifying the $\beta_{|}$ parameter (the parameter γ will not be affected by the stain rate or stretch temperature as it is not a property of deformation). We expect $\beta_{|}$ to decrease with increasing strain rate or decreasing stretch temperature as these effects should decrease the value of a at a given stretch ratio δ. However, due to the scarcity of our present knowledge on the kinetic effect on the chain deformation process, we shall refrain from speculating on the specific strain rate (or stretching temperature) dependence of $\beta_{|}$.

In summary, we have studied diffusion coefficients of camphorquinone in stretched PC films using the holographic grating relaxation technique. The diffusion coefficients, parallel and perpendicular to the direction of stretch, were measured as a function of the

stretch ratio. The diffusion coefficient along the stretching direction is found to increase with increasing stretch ratio, whereas the diffusion coefficient perpendicular the stretching direction decreases slightly with increasing stretching. The diffusion coefficient in the direction of stretch is found to slightly increase with the strain rate, but it decreases rapidly with increasing the stretching temperature above T_g. The anisotropic diffusion coefficients are interpreted in terms of a modified free volume theory.

Figure Caption:

Figure 1. Orientation of the PC films with respect to the laser beams for the LIHGR measurement.

Figure 2. Diffusion coefficients $D_{||}$ and $D_{\perp}$ plotted as a function of stretch ratio. Circles are experimental data. The curves are fit to the experimental data according to Eqs. (6) and (7).

Figure 3. Variation of $D_{||}$ with the strain rate drawn to 88% elongation.

Figure 4. Variation of $D_{||}$ with the temperature of stretch for the samples kept at 88% elongation.

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